

# In Situ Control of the Adsorption Species in CO<sub>2</sub> Hydrogenation: Determination of Intermediates and Byproducts

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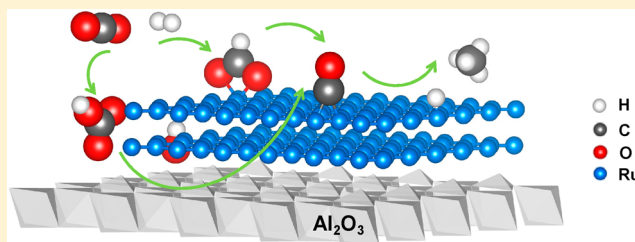
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## S Supporting Information

**ABSTRACT:** CO<sub>2</sub> hydrogenation over catalysts is a potentially exciting method to produce fuels while closing the CO<sub>2</sub> cycle and mitigating global warming. The mechanism of this process has been controversial due to the difficulty in clearly identifying the species present and distinguishing which are reaction intermediates and which are byproducts. We in situ manipulated the independent formation and hydrogenation of each adsorption species produced in CO<sub>2</sub> hydrogenation reaction over Ru/Al<sub>2</sub>O<sub>3</sub> using operando diffuse reflectance infrared Fourier transformation spectroscopy (DRIFTS) and executed a novel iterative Gaussian fitting procedure. The adsorption species and their role in the CO<sub>2</sub> hydrogenation reaction have been clearly identified. The adsorbed carbon monoxide (CO\*) of four reactive structures was the key intermediate of methane (CH<sub>4</sub>) production. Bicarbonate (HCO<sub>3</sub><sup>−</sup>\*), formed on the metal–support interface, appeared to be not only the primary product of CO<sub>2</sub> chemisorption but also a reservoir of CO\* and consisted of the dominate reaction steps of CO<sub>2</sub> methanation from the interface to the metal surface. Bidentate formate (Bi-HCOO<sup>−</sup>\*) formed on Ru under a certain condition, consecutively converting to CO\* to merge into the subsequent methanation process. Nonreactive byproducts of the reaction were also identified. The evolution of the surface species revealed the essential steps of the CO<sub>2</sub> activation and hydrogenation reactions which were inevitably initiated from HCO<sub>3</sub><sup>−</sup>\* to CO\* and finally from CO\* to CH<sub>4</sub>.



## 1. INTRODUCTION

CO<sub>2</sub> reduction by H<sub>2</sub> is a promising way to store hydrogen energy in hydrocarbons, producing synthetic fuels that exhibit the same energy density as fossil fuels to meet the increasing energy demands.<sup>1,2</sup> Moreover, the use of CO<sub>2</sub> as feedstock allows closure of the CO<sub>2</sub> cycle, reducing CO<sub>2</sub> emission and alleviating global warming. The mechanisms of CO<sub>2</sub> hydrogenation have been widely investigated on supported group VIII metals such as Ni, Ru, and Rh.<sup>3–8</sup> One of the principal analytical methods used is infrared spectroscopy, particularly diffuse reflectance infrared Fourier transformation spectroscopy (DRIFTS) for studying both the gaseous phase and the adsorption species on the catalyst surface. The main product is commonly found to be gaseous CH<sub>4</sub>. However, various reaction mechanisms have been proposed, referring to different intermediates. Gaseous CO and adsorbed CO\* were considered as important intermediates of CO<sub>2</sub> methanation because the well-known reversed water gas shift (RWGS) reaction could take place in the path of CH<sub>4</sub> production.<sup>9–12</sup> Some research has found that gaseous CO is not an intermediate as CO<sub>2</sub> was produced without visible occurrence of gaseous CO.<sup>13,14</sup> Instead, the adsorbed CO\*, which is formed via surface RWGS reaction, is more favorable to be the

intermediate as the adsorbed CO\* exhibits relation with CH<sub>4</sub> formation.<sup>15–19</sup> However, other research also supports that the adsorbed formate (HCOO<sup>−</sup>\*) is the intermediate rather than CO\*.<sup>20</sup> The mechanism of CO<sub>2</sub> hydrogenation is still controversial.

There are two key problems with the previous work: difficulties in the definitive determination of the species that appear during the reaction and difficulty with knowing whether a given species is an intermediate or a byproduct of CO<sub>2</sub> methanation.

To address the first problem, we resolved the peaks of the adsorbates using Gaussian fittings which were iteratively improved to produce a consistent view of the trends in observed species. To address the second problem, we controlled the formation of each adsorption species in situ, followed by reducing the obtained adsorption species individually in H<sub>2</sub> to monitor their role in the hydrogenation process. This allowed us to trace the origin and reaction path of each adsorption species and to determine the key

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intermediate of CO<sub>2</sub> methanation. We found that the essential pathway of CO<sub>2</sub> activation was CO<sub>2</sub> → HCO<sub>3</sub><sup>−</sup>\* → CO\* whether H<sub>2</sub> was present or not. The surface RWGS reaction and HCOO<sup>−</sup>\* contributed to CO\* formation only when the system had abundant CO<sub>2</sub> and H<sub>2</sub>. CO\* was the key intermediate of CO<sub>2</sub> methanation. Besides, the reactivities of the adsorption species were adsorption-structure-dependent.

## 2. EXPERIMENTAL SECTION

**Chemicals and Apparatus.** The experiments were performed on ground Ru/Al<sub>2</sub>O<sub>3</sub> (Sigma-Aldrich, 0.5 wt % loading on 3.2 mm pellets) or Al<sub>2</sub>O<sub>3</sub> (Sigma-Aldrich). The infrared spectra were recorded using a Bruker Tensor 27 spectrophotometer with a resolution of 2 cm<sup>−1</sup>, equipped with the Praying Mantis accessory and high-temperature reaction chamber (HVC) from Harrick Scientific for the diffuse reflectance infrared Fourier transformation spectroscopy (DRIFTS). The chamber was connected to He (purity 99.999%), H<sub>2</sub> (purity 99.999%), and CO<sub>2</sub> (purity 99.998%) gas lines and a turbomolecular pump. The tubing and the chamber were heated at 100 °C under vacuum overnight after loading the sample. The background pressure was 1 × 10<sup>−5</sup> mbar. The spectrophotometer was continuously flushed with clean dry compressed air.

**Sample Preparation.** Ru/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> was prereduced in the DRIFTS cell in H<sub>2</sub> flow with heating from room temperature (RT) to 350 °C at a heating rate of 2 °C/min and maintained at 350 °C for 4 h to remove the surface oxides on the Ru metal. The sample was then allowed to cool to RT in H<sub>2</sub> flow. A high vacuum of 1 × 10<sup>−5</sup> mbar was recovered after pumping.

**Experiments Performed.** Following the pretreatment, seven sets of experiments were done: **Exp. I** CO<sub>2</sub> hydrogenation reaction. This was initiated by mixing 200 mbar of CO<sub>2</sub> and 800 mbar of H<sub>2</sub> at RT and heated to 300 °C with a rate of 1 °C/min on both Ru/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. **Exp. II** CO<sub>2</sub> adsorption reaction. This was initiated by mixing 200 mbar of CO<sub>2</sub> and 800 mbar of He at RT, followed by heating to 300 °C with a rate of 1 °C/min on both Ru/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. **Exp. III** HCO<sub>3</sub><sup>−</sup>\* decomposition reaction. This was initiated by mixing 200 mbar of CO<sub>2</sub> and 800 mbar of He at RT, followed by pumping to high vacuum of 5 × 10<sup>−5</sup> mbar, then heating to 300 °C with a rate of 1 °C/min on Ru/Al<sub>2</sub>O<sub>3</sub>. **Exp. IV** CO\* hydrogenation. This was obtained directly from a HCO<sub>3</sub><sup>−</sup>\* decomposition experiment at 300 °C, followed by cooling to RT, then filling with 1 bar of H<sub>2</sub> and heating to 300 °C with a rate of 1 °C/min on Ru/Al<sub>2</sub>O<sub>3</sub>. **Exp. V** HCO<sub>3</sub><sup>−</sup>\* hydrogenation reaction. This was initiated by mixing 200 mbar of CO<sub>2</sub> and 800 mbar of He at RT, followed by pumping to high vacuum of 5 × 10<sup>−5</sup> mbar, then filling the cell with 1 bar of H<sub>2</sub> and heating to 300 °C with a rate of 1 °C/min on Ru/Al<sub>2</sub>O<sub>3</sub>. There are also two experiments which were done without reducing the surface: **Exp. VI** HCOOH adsorption. HCOOH was obtained from an external HCOOH droplet. The HCOOH droplet was added on the sample of Ru/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> in air. Afterward, the sample was pumped to low vacuum of 5 × 10<sup>−3</sup> mbar over 24 h at RT. **Exp. VII** HCOOH hydrogenation. To determine the hydrogenation properties of HCOOH on Ru/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, the samples were exposed to 1 bar of H<sub>2</sub> after Exp VI and then heated to 300 °C with a rate of 1 °C/min.

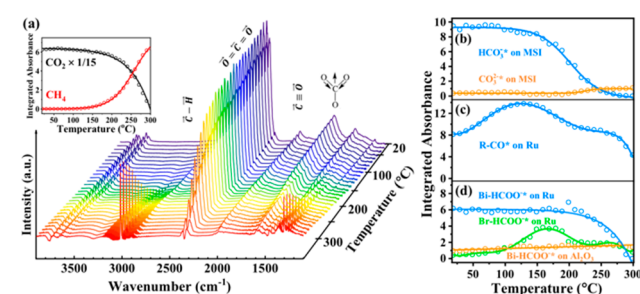
In addition, solid reference samples of Na<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, NaHCO<sub>3</sub>, and KHCO<sub>3</sub> were analyzed by transmission FT-IR to obtain the infrared bands of CO<sub>3</sub><sup>2−</sup> and HCO<sub>3</sub><sup>−</sup>.

**Gaussian Fittings.** Four regions were separately fitted: 2100–1800 cm<sup>−1</sup>, 1800–1530 cm<sup>−1</sup>, 1530–1420 cm<sup>−1</sup>, and 1420–1350 cm<sup>−1</sup>. The baseline of each region was taken as a linear function. The position, width, and height of each Gaussian contribution were all constrained. The initial values of these constraints were taken from a combination of an estimation of the peak ranges observed in the spectra and the measured peaks of the reference samples. These initial parameters were used to simulate all the peaks in these ranges from all the experiments. The results of a fitting run were used to give the new values of parameters and constraint ranges for the next fitting run. This process was iterated manually hundreds of times until two criteria were met: (1) all the peaks followed regular and physically meaningful trends as the reaction proceeded, and (2) subsequently fits did not change the parameters of the peak position, height, and width.

The combination of the measurement of the reference samples and the Gaussian fittings through the reaction coordination helped to identify and assign the observed peaks.

## 3. RESULTS AND DISCUSSION

**3.1. Correlations of Coexisting Adsorption Species in the CO<sub>2</sub> Hydrogenation Reaction.** In order to learn what species come out during CO<sub>2</sub> hydrogenation, we triggered CO<sub>2</sub> hydrogenation reaction on Ru/Al<sub>2</sub>O<sub>3</sub> by mixing CO<sub>2</sub> and H<sub>2</sub> followed by program heating (Exp. I). Figure 1(a) shows



**Figure 1.** (a) Infrared absorbance spectra with the insertion of CO<sub>2</sub> to CH<sub>4</sub> conversion during CO<sub>2</sub> hydrogenation (Exp. I) and evolution of adsorption species of (b) HCO<sub>3</sub><sup>−</sup>\* with a peak at 1650 cm<sup>−1</sup> and CO<sub>3</sub><sup>2−</sup>\* with a peak at 1450 cm<sup>−1</sup> located at MSI, (c) R-CO\* on Ru, and (d) Bi-HCOO\* on Ru, Br- and Br-HCOO\* on Ru, and Bi-HCOO\* on Al<sub>2</sub>O<sub>3</sub>. In (b)–(d), circles are the original data of integrated peak intensity from Gaussian fittings, and the lines are the nonlinear fittings of those original data.

the main reaction of CO<sub>2</sub> converting to CH<sub>4</sub> from 100 °C. The variations in the complex peaks below 2200 cm<sup>−1</sup> suggest the development of adsorption species from CO<sub>2</sub> and H<sub>2</sub> coadsorption during the hydrogenation reaction. The peaks were distinguished in three regions: C–O stretching of adsorbed carbon monoxide (CO\*) between 2100 and 1800 cm<sup>−1</sup>; O–C–O stretching of adsorbed bicarbonates (HCO<sub>3</sub><sup>−</sup>\*), carbonates (CO<sub>3</sub><sup>2−</sup>\*), and formate (HCOO<sup>−</sup>\*) between 1700 and 1400 cm<sup>−1</sup>; and C–H and O–H bending between 1400 and 1200 cm<sup>−1</sup> (Figure 1(a)). To identify the infrared peaks, we measured reference samples of carbonates, bicarbonates, and surface formic acid on Ru/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> (Figures S1 and S2). More importantly, we resolved the peaks of the adsorbates of each reaction using Gaussian fittings

**Table 1.** Vibrational Modes and Infrared Peak Positions ( $\text{cm}^{-1}$ ) of the Reference Samples and the Reaction Species from This Work<sup>a</sup>

species	C–H as. str.	C–H b.	C=O str.	O–C–O as. str.	O–C–O s. str.	O–C–O b.	O–H b.	C–OH str.
$\text{CO}_3^{2-}$	--	--	1776	1454	1454	880	--	--
$\text{CO}_3^{2-*bc23}$	--	--	--	1500	1450	--	--	--
$\text{HCO}_3^-$	--	--	1695	1650, 1630	1402, 1371	--	1305	1007
$\text{HCO}_3^{*-bc20,23-27}$	--	--	1690	1650	1440	--	1230	--
$\text{HCOOH}^{c28-30}$	2940, 2871	1415	1748, 1670	1620, 1560 (on $\text{Al}_2\text{O}_3$ )	1405, 1360	--	1220	970
Bi- $\text{HCOO}^{*-bd}$ on Ru	2913, 2895, 2870	1390	1720	1620	1405	--	1220	970
Br- $\text{HCOO}^{*-bd}$ on Ru	2913, 2895, 2870	1390	1720	1590	1375	--	1220	970
Bi- $\text{HCOO}^{*-bd}$ on $\text{Al}_2\text{O}_3^{c31}$	2918, 2895, 2870	1387	1710	1560	1360	--	1230	970
species	C $\equiv$ O as. str.							
linear- $\text{CO}^{*b}$ on Ru <sup><math>\delta+c26,30,32-35</math></sup>	2060							
linear- $\text{CO}^{*b}$ on Ru <sup><math>0c26,30,32-35</math></sup>	2035							
linear- $\text{CO}^{*b}$ on Ru <sup><math>0/\text{Ru}^{\delta+c26,30,32-35}</math></sup>	2015							
bridged- $\text{CO}^{*b}$ on Ru <sup><math>c26,30,32-35</math></sup>	1990, 1950, 1905							
gaseous CO	2150							

<sup>a</sup>str.: stretching. as.: asymmetric. s.: symmetric. b.: bending. (w): weak. <sup>b</sup>\* indicates adsorbed state. <sup>c</sup>The corresponding bond vibrations and infrared peak positions are comparable to the given references. <sup>d</sup>The way to distinguish bidentate and bridged structures of formate is as follows: bidentate- $\text{HCOO}^{*-}$  has the splitting value of O–C–O asymmetric ( $\nu_{as}$ ) and symmetric ( $\nu_s$ ) stretching,  $\Delta\nu = \nu_{as} - \nu_s$ , less than  $220 \text{ cm}^{-1}$ , and bridged- $\text{HCOO}^{*-}$  has  $\Delta\nu$  in the range of  $220\text{--}280 \text{ cm}^{-1}$ .<sup>36</sup>

(Figure S3). The peak assignments are summarized in Table 1 based on the combination of reference peaks and Gaussian fittings.

At RT, four types of adsorption species were formed during the  $\text{CO}_2$  hydrogenation reaction on Ru/ $\text{Al}_2\text{O}_3$ :  $\text{HCO}_3^{*-}$ ,  $\text{CO}_3^{2-*}$ ,  $\text{CO}^*$ , and  $\text{HCOO}^{*-}$ .  $\text{HCO}_3^{*-}$  were formed by reaction of  $\text{CO}_2$  with the surface hydroxyl groups on the  $\text{Al}_2\text{O}_3$  support following the  $\text{H}_2$  pretreatment. The intensity of  $\text{HCO}_3^{*-}$  was larger on Ru/ $\text{Al}_2\text{O}_3$  than on bare  $\text{Al}_2\text{O}_3$ , and  $\text{HCO}_3^{*-}$  on  $\text{Al}_2\text{O}_3$  could not be continuously formed from  $\text{CO}_2$  on  $\text{Al}_2\text{O}_3$  (Figures S4 and S5), indicating the adsorption of  $\text{HCO}_3^{*-}$  is increased by the metal–support interface (MSI). As shown in Figure 1(b), during the temperature ramp the concentration of  $\text{HCO}_3^{*-}$  was initially constant and started to decrease above about  $150^\circ\text{C}$ .  $\text{CO}_3^{2-*}$  increased gradually with increasing temperature above  $200^\circ\text{C}$ , and the increase most likely came from  $\text{HCO}_3^{*-}$  deprotonation. Assuming that the peak intensities for O–C–O stretching are similar in  $\text{HCO}_3^{*-}$  and  $\text{CO}_3^{2-*}$  at the same site and coverage, the much lower intensity of  $\text{CO}_3^{2-*}$  indicates that only some of the  $\text{HCO}_3^{*-}$  decomposed to  $\text{CO}_3^{2-*}$ , and the remaining  $\text{HCO}_3^{*-}$  molecules were consumed in other processes, for instance, desorption or decomposition.

Reactive  $\text{CO}^*$  ( $\text{R-CO}^*$ ) with the peaks at 2015, 1990, 1950, and  $1905 \text{ cm}^{-1}$  (Table 1 and Figure S6) increased from RT up to  $150^\circ\text{C}$  (Figure 1(c)) and then decreased, indicating that its production was slower than its consumption above  $150^\circ\text{C}$ . At  $220^\circ\text{C}$ ,  $\text{R-CO}^*$  concentration leveled off, possibly because a new route of  $\text{R-CO}^*$  production became active. Nevertheless, linear- $\text{CO}^*$  on Ru<sup>0</sup> at  $2035 \text{ cm}^{-1}$  (Table 1) remained constant throughout the entire experiment, indicating the inert character of this species (Figure S6). It has been reported that hydrogen-perturbed CO could locate in the range between  $1840$  and  $1700 \text{ cm}^{-1}$  and could be  $\text{H}_2\text{CO}$  species or carbonyl hydrides and formyl/formaldehyde.<sup>21,22</sup> In our case, we did not have peaks between that region as shown in Figure S6. The discrepancy between the reference and our work could be originated by the different effects of different catalyst surfaces which are sensitive/selective to the different adsorption species.

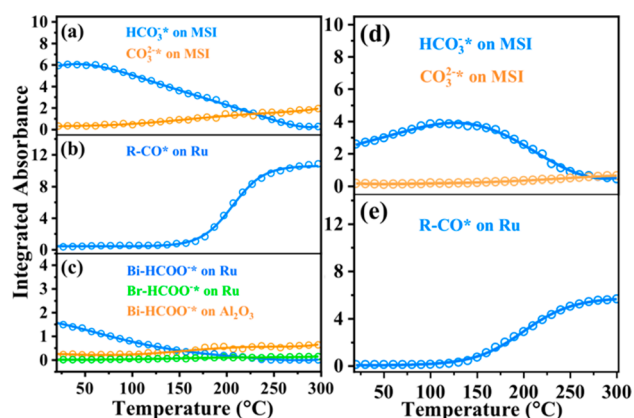
$\text{HCOO}^{*-}$  is present in three forms: bidentate on Ru with a high frequency of  $1620 \text{ cm}^{-1}$ , bridged on Ru with a frequency of  $1590 \text{ cm}^{-1}$ , and bidentate on  $\text{Al}_2\text{O}_3$  with a frequency of  $1560 \text{ cm}^{-1}$  (Table 1). Bidentate- $\text{HCOO}^{*-}$  (Bi- $\text{HCOO}^{*-}$ ) on Ru was abundant and stable up to  $220^\circ\text{C}$ , after which it was consumed and completely disappeared at  $300^\circ\text{C}$ . Conversely, bridged- $\text{HCOO}^{*-}$  (Br- $\text{HCOO}^{*-}$ ) on Ru increased from 70 to  $160^\circ\text{C}$ , followed by a slow decrease (Figure 1(d)). Bidentate- $\text{HCOO}^{*-}$  (Bi- $\text{HCOO}^{*-}$ ) on  $\text{Al}_2\text{O}_3$  showed only one weak peak at  $1560 \text{ cm}^{-1}$  (Figure 1(d)). The slight increase in production of this species, instead of consumption, indicates it is not reactive during  $\text{CO}_2$  hydrogenation.

**3.2. Unraveling the Roles of Individual Species Using in Situ Control.** The temperature-dependent evolution of the above-mentioned species shows correlations with the  $\text{CO}_2$  methanation reaction. However, their simultaneous existence makes the determination of their origins and roles in the reaction equivocal. To unravel these mysteries, we isolate the adsorption species step by step in the following sections.

**3.2.1. Interactions of  $\text{CO}_2$  and the Surface.** We first investigated the interactions between  $\text{CO}_2$  and the surface by replacing  $\text{H}_2$  with He, keeping all other conditions the same (Exp. II). The results are shown in Figure 2(a)–(c). At RT,  $\text{HCO}_3^{*-}$  was the main species formed when the surface was exposed in  $\text{CO}_2$ , indicating that it is the primary product of  $\text{CO}_2$  adsorption (Figure 2(a)).  $\text{HCO}_3^{*-}$  decreased almost linearly with increasing temperature after  $50^\circ\text{C}$ . Simultaneously,  $\text{CO}_3^{2-*}$  increased almost linearly with increasing temperature. These trends are similar to those in the  $\text{CO}_2$  hydrogenation reaction (Figure 1(b)). The higher ratio of  $\text{CO}_3^{2-*}/\text{HCO}_3^{*-}$  for  $\text{CO}_2$  adsorption than that for  $\text{CO}_2$  hydrogenation reflects the more favorable deprotonation of  $\text{HCO}_3^{*-}$  in  $\text{H}_2$ -deficient conditions.

All the  $\text{CO}^*$  showed the same peaks as those in  $\text{CO}_2$  hydrogenation except for a  $25 \text{ cm}^{-1}$  redshift of the peak of linear- $\text{CO}^*$  at  $2035 \text{ cm}^{-1}$  (Figure S7). This redshift was probably due to the adsorption of linear- $\text{CO}^*$  onto the oxidized metal surface ( $\text{Ru}^{\delta+}$ ) in a hydrogen-deficient environment. This linear- $\text{CO}^*$  at  $2035 \text{ cm}^{-1}$  showed no change in the whole process, as same insensitiveness as in the  $\text{CO}_2$





**Figure 2.** (a)  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , (b)  $\text{R-CO}^*$ , (c) three structural  $\text{HCOO}^-$  during  $\text{CO}_2$  adsorption reaction (Exp. II), (d)  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , and (e)  $\text{R-CO}^*$  during  $\text{HCO}_3^-$  decomposition (Exp. III). The peak positions were the same as in Figure 1. The circles are the original data of integrated peak intensity from Gaussian fittings, and the lines are the nonlinear fittings of those original data.

hydrogenation reaction (Figure S7). Notably,  $\text{R-CO}^*$  increased above 150 °C (Figure 2(b)). This increase in  $\text{R-CO}^*$  production explains the plateau in  $\text{R-CO}^*$  concentration starting at 220 °C in  $\text{CO}_2$  hydrogenation (Figure 1(c)). However, whether these  $\text{CO}^*$  were produced from the decomposition of  $\text{CO}_2$  or  $\text{HCO}_3^-$  is not clear yet and needed further controlling experiments.

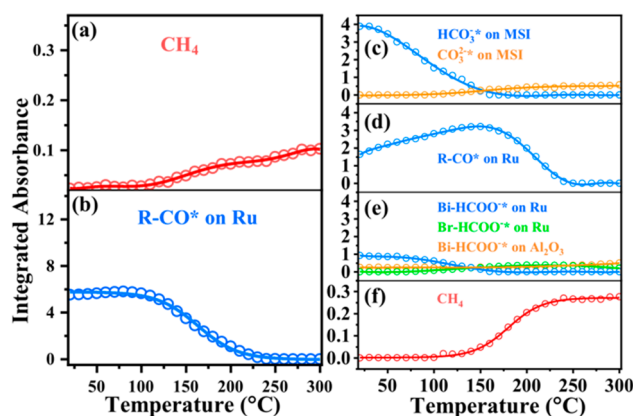
$\text{Bi-HCOO}^-$  on Ru at RT had much weaker intensity (Figure 2(c)) than the corresponding intensity when  $\text{H}_2$  was present (Figure 1(d)). The intensity decreased with increasing temperature until complete disappearance at 220 °C. We speculate that  $\text{Bi-HCOO}^-$  is not formed from  $\text{HCO}_3^-$  since  $\text{HCOO}^-$  does not increase when  $\text{HCO}_3^-$  decreases. Rather,  $\text{Bi-HCOO}^-$  must be formed by  $\text{CO}_2$  reacting with adsorbed H atoms on the surface. Thus, we conclude that there must be a small amount of residual H atoms present in this experiment and that the small concentration of H explains the small concentration of  $\text{Bi-HCOO}^-$ .  $\text{Br-HCOO}^-$  on Ru was almost invisible, indicating that  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}^*$  do not form  $\text{Br-HCOO}^-$  in a hydrogen-deficient environment.  $\text{Bi-HCOO}^-$  on  $\text{Al}_2\text{O}_3$  slightly increased above 150 °C when  $\text{Bi-HCOO}^-$  on Ru disappeared possibly due to migration of  $\text{Bi-HCOO}^-$  on Ru to  $\text{Al}_2\text{O}_3$  support.<sup>15</sup>

**3.2.2. In Situ Isolation and Decomposition of  $\text{HCO}_3^-$ .** To determine whether  $\text{CO}^*$  was formed from the decomposition of  $\text{CO}_2$  or  $\text{HCO}_3^-$ , we pumped out the gases after  $\text{CO}_2$  adsorption at RT (Exp. III). In this way, we produced a surface exclusively covered by  $\text{HCO}_3^-$  at RT. The catalyst was then heated. Broadly speaking, during heating  $\text{HCO}_3^-$  decreased (Figure 2(d)) starting from 130 °C, and there was a corresponding increase in  $\text{R-CO}^*$  concentration (Figure 2(e)), excluding the inert linear- $\text{CO}^*$  at 2065  $\text{cm}^{-1}$  (Figure S8). Thus, we conclude that the  $\text{R-CO}^*$  originates from  $\text{HCO}_3^-$  and not from  $\text{CO}_2$ . The 20 °C lower temperature than the onset temperature of  $\text{R-CO}^*$  formation in  $\text{CO}_2$  adsorption reaction (Figure 2(b)) is probably the reason for released active sites in a high vacuum. We currently do not have an explanation for the increase in  $\text{HCO}_3^-$  at the beginning of the temperature ramp, but the broad conclusion stands.

**3.2.3. In Situ Isolation and Hydrogenation of  $\text{CO}^*$ .** To find out which adsorption species can react to form  $\text{CH}_4$ , we

hydrogenated them separately by preparing them individually with in situ control.

We first isolated all the  $\text{CO}^*$  in situ from  $\text{HCO}_3^-$  decomposition following the process shown in Figure 2(d) and (e) and cooling to RT. One bar of  $\text{H}_2$  was then filled followed by program heating (Exp. IV). As shown in Figure 3(a) and (b),  $\text{R-CO}^*$  decreased, and  $\text{CH}_4$  increased starting at



**Figure 3.** (a) Production of  $\text{CH}_4$  and (b) reduction of  $\text{CO}^*$  during  $\text{R-CO}^*$  hydrogenation (Exp. IV). Evolution of (c)  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , (d)  $\text{R-CO}^*$ , (e) three structural  $\text{HCOO}^-$ , and (f)  $\text{CH}_4$  during  $\text{HCO}_3^-$  hydrogenation (Exp. V). The peak positions were the same as in Figure 1. The circles are the original data of integrated peak intensity from Gaussian fittings, and the lines are the nonlinear fittings of those original data.

120 °C. Note that this onset temperature is 20 °C higher than that observed in the  $\text{CO}_2$  hydrogenation reaction (Figure 1(a)) probably because of the lower  $\text{R-CO}^*$  concentration in this case. Linear- $\text{CO}^*$  at 2040  $\text{cm}^{-1}$  was still inert in this hydrogenation process (Figure S9). Thus, we conclude  $\text{R-CO}^*$  is clearly an intermediate in the  $\text{CH}_4$  formation reaction, while the linear- $\text{CO}^*$  above 2035  $\text{cm}^{-1}$  is a byproduct.

**3.2.4. In Situ Isolation and Hydrogenation of  $\text{HCO}_3^-$ .** Next, we investigate whether  $\text{HCO}_3^-$  is an intermediate.  $\text{HCO}_3^-$  was obtained in situ from  $\text{CO}_2$  adsorption followed by pumping to high vacuum at RT (Exp. V). As shown in Figure 3(c)–(e), when the sample was heated in  $\text{H}_2$ ,  $\text{HCO}_3^-$  concentration decreased immediately until completely consumed at 150 °C. Meanwhile,  $\text{R-CO}^*$  and  $\text{Bi-HCOO}^-$  on Ru were immediately produced at RT. There is a corresponding increase in the concentration of  $\text{R-CO}^*$  which is the result of surface RWGS reaction triggered by  $\text{HCO}_3^-$  hydrogenation at MSI. Thus, we conclude that  $\text{HCO}_3^-$  is an intermediate in the overall reaction, producing  $\text{CO}^*$  which is subsequently converted to  $\text{CH}_4$  (Figure 3(f)).

**3.2.5. Role of  $\text{HCOO}^-$ .** Finally, we consider whether  $\text{HCOO}^-$  is an intermediate. Unfortunately, we were unable to produce isolated  $\text{HCOO}^-$  by in situ control because  $\text{HCO}_3^-$  was always present when  $\text{HCOO}^-$  was produced. Nonetheless, we have evidenced that  $\text{Bi-HCOO}^-$  on Ru formed in our in situ control is a reaction intermediate. Figure 1(d) shows that in the  $\text{CO}_2$  hydrogenation reaction  $\text{Bi-HCOO}^-$  on Ru formed from  $\text{CO}_2$  hydrogenation and was consumed in the same shape of the reactive species of  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{R-CO}^*$  above 220 °C. This consumption could involve the formation reaction of  $\text{CO}^*$  or  $\text{CH}_4$ . In Figure 3(e), when there was no  $\text{CO}_2$ ,  $\text{Bi-HCOO}^-$  on Ru was formed by the previous step of  $\text{CO}_2$  adsorption reacting with residual hydrogen on the

surface. Bi-HCOO<sup>−</sup>\* on Ru started to decrease at a 40 °C lower temperature than the onset temperature of CH<sub>4</sub> formation. Therefore, we conclude that Bi-HCOO<sup>−</sup>\* on Ru is reduced by hydrogen to form CO\* instead of directly to CH<sub>4</sub>. Additionally, Bi-HCOO<sup>−</sup>\* on Ru could convert to the bridged form on Ru from 70 to 160 °C as illustrated in Figure 1(d) and Figure 3(e). This Br-HCOO<sup>−</sup>\* on Ru could be reduced above 160 °C but not completely when it was abundant (Figure 1(d)). However, it kept constant above 160 °C when it had low concentration. This implies that Br-HCOO<sup>−</sup>\* on Ru has a high activation energy of hydrogenation. Bi-HCOO<sup>−</sup>\* on Al<sub>2</sub>O<sub>3</sub> was a byproduct as it always slowly increased by the migration of HCOO<sup>−</sup>\* on Ru in all the experiments.

The distinct reactivities between the HCOO<sup>−</sup>\* of different adsorption structures on Ru can be understood by the atomic structure of the surface. The distance between neighboring Ru atoms in a hexagonal structure is 2.71 Å, while the distance between the two oxygen atoms of formate is 2.20 Å. These two comparable distances facilitate adsorption of the bridged structure of formate to the surface of the bulk Ru, where the two oxygen atoms bind to two adjacent Ru atoms. A larger distance between Ru atoms, e.g., at the edge or defect where some Ru atoms are isolated, is required to accept Bi-HCOO<sup>−</sup>\* on Ru so that two oxygen atoms bind to one Ru atom. Therefore, the bulk sites of the surface result in the stable Br-HCOO<sup>−</sup>\* on Ru, and the edge or defect centers promote the high reactivity of Bi-HCOO<sup>−</sup>\* on Ru.

We also prepared isolated HCOO<sup>−</sup>\* by ex situ application of a drop of HCOOH to the sample in air followed by pumping to vacuum. All the forms of HCOO<sup>−</sup>\* on Ru/Al<sub>2</sub>O<sub>3</sub> were reactive and started to form CO\* above 150 °C (Figure S2). Above 220 °C, Bi-HCOO<sup>−</sup>\* on Ru and on Al<sub>2</sub>O<sub>3</sub> were substantially reduced, leading to CO\* formation slowing down and CH<sub>4</sub> formation. Br-HCOO<sup>−</sup>\* on Ru was not reduced completely. The ex situ experiment supports the conclusion that Bi-HCOO<sup>−</sup>\* on Ru is a reaction intermediate, and Br-HCOO<sup>−</sup>\* on Ru possesses high activation energy of reduction; however, on the other hand, it showed a discrepancy with the in situ experiment where Bi-HCOO<sup>−</sup>\* on Al<sub>2</sub>O<sub>3</sub> was also reactive. The discrepancy is not surprising given that the ex situ experiment involved exposure to air and the high acidity of the sample. The discrepancy points out the danger of obtaining misleading results by ex situ preparation.

#### 4. CONCLUSIONS

The results we have just described can be understood in terms of the reaction mechanisms summarized in Figure 4. There are two pathways to CO<sub>2</sub> methanation. One is initiated by HCO<sub>3</sub><sup>−</sup>\* formation, illustrated by the green arrow. The other is initiated by the formation of Bi-HCOO<sup>−</sup>\* on Ru, illustrated by the orange arrow. In the HCO<sub>3</sub><sup>−</sup>\* pathway, first, HCO<sub>3</sub><sup>−</sup>\* is formed at RT when CO<sub>2</sub> adsorbs and reacts with the surface hydroxyl groups on the metal–support interface which originated from the H<sub>2</sub> prereduction of the surface. Next, the HCO<sub>3</sub><sup>−</sup>\* is reduced to CO\* by hydrogen at RT. HCO<sub>3</sub><sup>−</sup>\* also produces CO\* via thermal decomposition above 130 °C in high vacuum and above 170 °C in a CO<sub>2</sub>- and H<sub>2</sub>-rich environment. The temperature shift is due to competition for adsorption sites. In the Bi-HCOO<sup>−</sup>\* pathway, the first step is the reaction of CO<sub>2</sub> and hydrogen to produce Bi-HCOO<sup>−</sup>\* on Ru at RT. This species then reacts with hydrogen to produce CO\* on Ru at RT. Alternatively, Bi-HCOO<sup>−</sup>\* on Ru converts

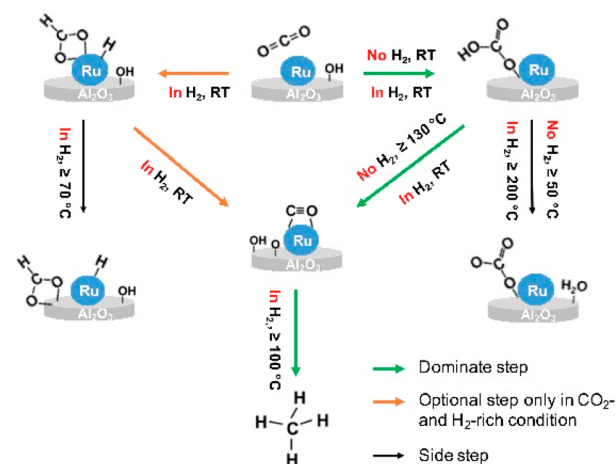


Figure 4. Schema of the hydrogenation steps of CO<sub>2</sub> on Ru/Al<sub>2</sub>O<sub>3</sub>.

to more stable Br-HCOO<sup>−</sup>\* on Ru which has a higher activation energy to reaction and does not fully convert under our conditions (not shown in the figure). In both pathways, the final process is the hydrogenation of R-CO\* to CH<sub>4</sub> above 100 °C. R-CO\* is consequently a key intermediate in CO<sub>2</sub> methanation.

In addition to the pathways leading to CH<sub>4</sub> formation, there are also notable side reactions that lead to nonreactive byproducts. As shown by the black arrow on the right side of Figure 4, HCO<sub>3</sub><sup>−</sup>\* decomposes to CO<sub>3</sub><sup>2−</sup>\* at 50 °C in a hydrogen-deficient environment and at 200 °C in a hydrogen-rich environment. The black arrow on the left side of Figure 4 shows that Bi-HCOO<sup>−</sup>\* on Ru converts to Bi-HCOO<sup>−</sup>\* on Al<sub>2</sub>O<sub>3</sub>. Besides, linear-CO\* on Ru<sup>0</sup> forms along with R-CO\* but also is insensitive to the hydrogenation reaction (not shown in the figure).

In summary, we unraveled the surface reaction mechanism of CO<sub>2</sub> hydrogenation via in situ control of the individual formation and hydrogenation of each adsorption species in operando DRIFTS combined with iterative Gaussian fitting. CO<sub>2</sub> → HCO<sub>3</sub><sup>−</sup>\* → CO\* → CH<sub>4</sub> is the dominate reaction step which takes place from the metal–support interface to the metal surface. This gives us the effective pathway and surface sites for CO<sub>2</sub> methanation.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b06508.

Infrared spectra of all the experiments, the evolution of each vibrational mode of each species, and the explanation of bicarbonate adsorption at MSI are illustrated (PDF)

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##### Notes

The authors declare no competing financial interest.

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